Two Photon Dissociation of Benzene, Phenylacetylene, and Benzaldehyde at 243 nm: Translational Energy Releases in the H Atom Channel

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Hydrogen atom production channels from photodissociation of benzene, phenylacetylene, and benzaldehyde at 243 nm have been investigated by detecting H atoms using two photon absorption at 243.2 nm and induced fluorescence at 121.6 nm. Translational energies of the H atoms were measured by Doppler broadened H atom spectra. By absorption of two photons at 243 nm, the H atoms are statistically produced from benzene and phenylacetylene whereas the H atoms from the aldehyde group in benzaldehyde are produced from different pathways. The possible dissociation mechanisms are discussed from the measured translational energy releases.

Keywords : Dissociation, Benzene, Translational energy.

Introduction

Hydrogen atoms can be detected by direct one photon absorption or emission of light at the Lyman-α wavelength of 121.6 nm *via* the 1s-2p transition.[1] Alternatively, two photon absorption in H at 205.14 nm reaches 3s and 3d state and emission in the red (the Balmer-α line at 656.2 nm) resulting from relaxation to the 2p state or the emission from the subsequent 2p $\rightarrow$ 1s relaxation at 121.6 nm can be used for the detection of H atoms.[2,3] The spectra of H can be obtained either by detection of light or by detection of hydrogen ions generated from (2+1) photon absorption at 205.14 nm. The two photon absorption in H at 243.2 nm cannot directly reach the 2p state but reaches the 2s state followed by quenching to the 2p state, which emits fluorescence at 121.6 nm resulting from the relaxation to the 1s state. Taking advantage of this technique, the spectra of H produced from photodissociation of molecules containing H at 205.14 or 243.2 nm can be obtained by the single frequency light.[4]

Studies on the photodissociation dynamics are of fundamental importance in understanding electronic structures of the molecules because the process is governed by the electronically excited state and the corresponding potential energy surfaces along the reaction coordinates. In order to understand the dynamics of the reaction, certain physical properties such as energy distribution among products should be measured because sophisticated theories describing the dynamics of the reaction can predict the experimentally measurable quantities, from which the detailed process can be explored. In particular, the translational energies of the products can be measured from the Doppler broadened spectra of the product when the absorption and/or emission in the products take place in an easily accessible spectral region. From the detailed dynamics, the potential energy surfaces and properties of the excited states can be studied.

Photochemistry and photophysics of benzene have long been subjects of interest.[5-7] It has been known that upon UV irradiation, rapid internal conversion to lower electronic states results in benzene in the vibrationally hot ground state. In fact, the lifetimes of benzene in the S_2 and S_1 state were directly measured to be 40 fs and 5 ps, respectively.[8] The dissociation of this hot benzene produced by the photon absorption at 193 and 248 nm was investigated.[9] The dissociation rate was measured to be 1×10^5 s^{-1} at 193 nm, which depends upon the internal energy of the parent molecule.[10] In addition, the major dissociation product was identified to be H atoms whereas H_2 and ring opening products were minor.

In this report, the translational energies of H produced from the dissociation of benzene excited by two photon absorption at 243 nm were measured by the Doppler broadened laser induced fluorescence spectra of H. In addition, the photodissociation dynamics of H from phenylacetylene and benzaldehyde was also investigated.

Experimental Section

The experiments were performed in a flow cell whose pressure was maintained at around 1×10^{-3} Torr without the sample. The gaseous samples were slowly flowed through the cell at pressures of about 100 mTorr controlled with needle valves. The photolysis and probe light was introduced to the cell through quartz windows and the resulting fluorescence was detected through a LiF window at a right angle to the light beam. The liquid samples with stated purity higher than 99% were purchased from Aldrich and used without further purification.

The photolysis and probe light, that is, 243.2 nm light was a frequency-doubled out put of a dye laser (Lumonics HD-500) pumped by the third harmonic of an Nd:YAG laser (Lumonics YM-800). The sample molecules were photodis-

sociated at 243.2 nm and the fragment H atoms absorbed two photons of the same light within the pulse and reached the 2s state. The H atoms were then quenched to the 2p state followed by relaxation to the ground state resulting in Lyman-α fluorescence at 121.6 nm. The resulting fluorescence was detected by a solar blind photomultiplier tube (Hamamatsu R1259). In order to increase the S/N ratio in the spectra, a Lyman-α filter was placed and dry nitrogen was flowed between the viewing window and the PMT. The detected signal was fed to boxcars and signal processors and stored in a PC.

Since the present experiment needed at least three photons to detect the fragment H atoms, the light was focused with a lens. In order to avoid saturation in the observed H atom spectra, the lenses of various focal lengths were tested and power dependence was studied. The linewidth of the laser beam was 0.07 cm^{-1} in the visible measured from the rotationally resolved gaseous I_2 spectra at ambient temperature. This linewidth was deconvoluted from the measured Doppler line profiles to measure the width of the spectra.

Results

Figure 1(a) displays the spectra of H and D produced from the 1:1 mixture of benzene and benzene-d_6. To ensure that the observed H atom spectra should not be from any impurities in the system but from benzene, D from benzene-d_6 was measured. The spectra of H and D from 1,3,5-benzene-d_3 are also displayed in Figure 1(b).

Since the experiment has been performed by so-called one color, that is, pump-probe by the same light and the light from the dye laser output is horizontally polarized, the polarization direction of the dissociating light, ε_d is conse-

a) $C_6H_6 + C_6D_6$

b) C_6H_6-$d_{1,3,5}$

Figure 1. H(D) atom spectra from photodissociation of (a) 1:1 mixture of benzene and benzene-d_6 (b) 1,3,5-benzene-d_3 at 243 nm.

quently perpendicular to the probe direction, k_p. However, judging from the Gaussian profiles observed in the spectra, we assumed no polarization dependence of the H atom production channels although we could not attempt a different experimental geometry such as $\varepsilon_d \parallel k_p$. In addition, as will be mentioned in the Discussion, since the H atoms are not produced from the direct photodissociation but produced from the slow unimolecular dissociation in the ground state resulting from internal conversion, it is believed that there is no initial polarization dependence and thus isotropic distribution of the H atoms can be assumed. In this case, the relations, $<\upsilon_x^2> = <\upsilon_y^2> = <\upsilon_z^2>$ and thus $<E_H> = 1/2\, m_H(<\upsilon_x^2> + <\upsilon_y^2> + <\upsilon_z^2>) = 3/2\, m_H <\upsilon_z^2>$ hold. Then, from the observed one dimensional Doppler broadened spectra, translational energies of the H (D) atoms were measured from the second moment of the spectra using the equation

$$<E_H> = 3 m_H <\upsilon_z^2>/2 = 3\, m_H <(\nu-\nu_0)^2>(c/\nu_0)^2/2$$

where ν_0 is the center frequency of the spectrum, υ_z is the velocity along the probe direction, and c is the speed of light. The center-of-mass translational energy releases were calculated and are listed in Table 1. The spectra of H and D from benzaldehyde-d (C_6H_5COD) and phenylacetylene-d ($C_6H_5C\equiv CD$) are shown in Figure 2(a) and 2(b), respectively. From the spectra, the translational energy releases in the systems were measured and are also listed in the table.

Since the difference in the photon energy between the H and D atom production is about 25 cm^{-1}, the same photolysis probability in this spectral region could be assumed. Also, since the photon energy around 243 nm is larger than 40,000 cm^{-1}, it is assumed that the contribution from this 25 cm^{-1} difference to the translational energy release should be negligible.

In order to clarify the dissociation mechanism, the power dependences of the fluorescence signals were studied. The log of the signals *vs.* the log of laser intensities were linear with the slopes around 4.2 ± 0.2 in all cases studied and showed saturation at higher laser intensities (Figure 3). These results imply two photon absorption for dissociation followed by two photon probe of H.

The dissociation energies of H from the parent molecules have not been reported except for benzene. Thus, *ab initio* calculations were performed to obtain heats of formation of the molecules involved. The B3LYP calculations were carried out with 6-31G(2df,3pd) basis sets using the GAUSSIAN program package.[11] The calculated heat of formation of benzaldehyde (-7.9 kcal/mol) is comparable to the reported value in the literature, -7.4 kcal/mol[12] and the similar
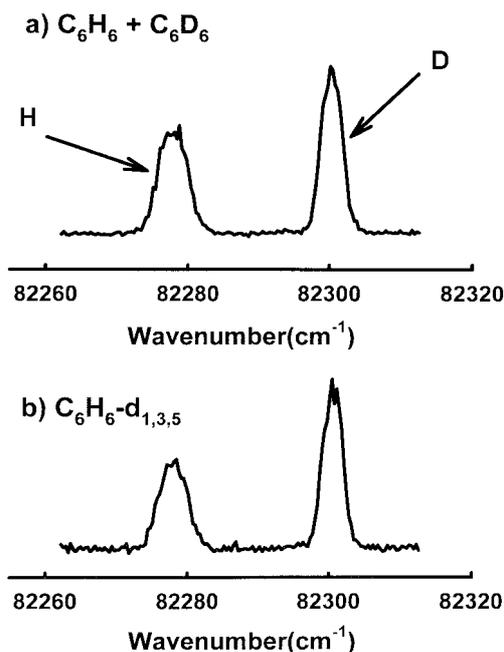
Table 1 Translational energy releases in the H atom channel from photodissociation of benzene, phenylacetylene, and benzaldehyde at 243 nm

	$C_6H_6 : C_6D_6$		C_6H_5CCD		C_6H_5COD	
	H	D	H	D	H	D
$<E_T>$ kJ/mol	70.3	70.8	72.8	73.5	74.2	82.7

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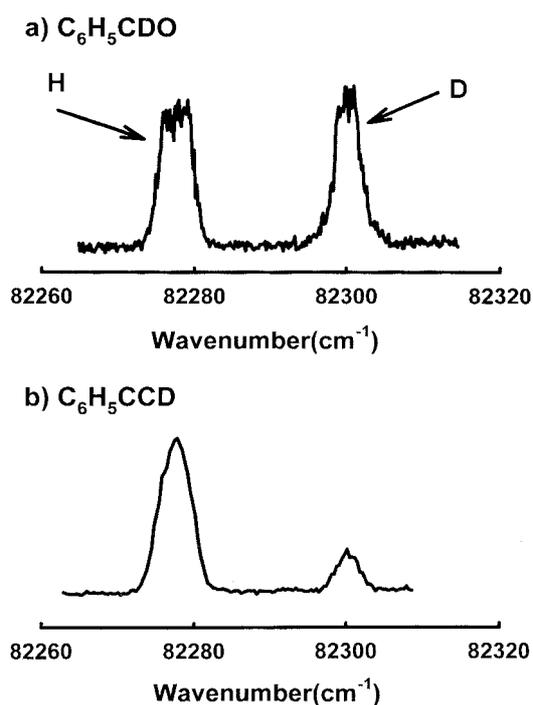
a) C₆H₅CDO


b) C₆H₅CCD

Figure 2. H(D) atom spectra from photodissociation of (a) C_6H_5COD and (b) C_6H_5CCD at 243 nm.
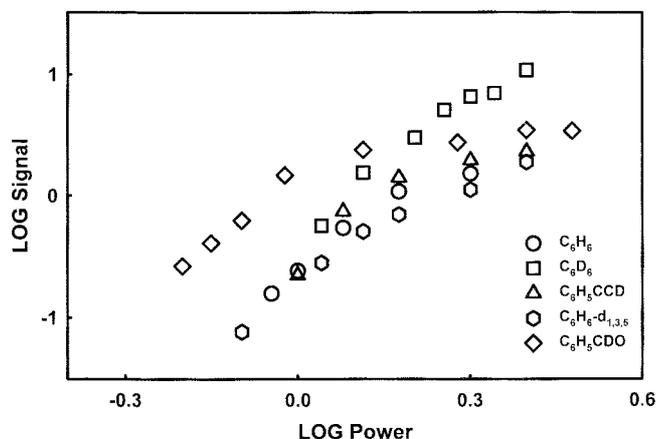

Figure 3. log-log plots of H(D) atom signals vs. laser intensities produced from the photodissociation of benzene, phenylacetylene, and benzaldehyde at 243 nm. The plots show linear slopes of 4.2 ± 0.3 at the low laser intensities.

accuracies are expected for the rest of the values from the calculation. Then, the dissociation energies were estimated from the calculated heats of formation.

Discussion

H from benzene: The major primary photochemical process from benzene has been known to produce H and phenyl radicals upon absorption of the UV light. The quantum yield of this channel was measured to be 0.8 at 193 nm.[9] The lifetimes of benzene in the S_1 and S_2 states were directly measured by a femtosecond pump-probe technique. From the initial excitation at 200 nm, the decay from the S_2 state

with 40 fs lifetime was measured due to internal conversion to the S_1 state followed by internal conversion to the ground state in 5-10 ps.[8] Thus, it has been suggested that the H atom production takes place in the hot ground state.

The dissociation of H from benzene is

$$C_6H_6 \rightarrow H + C_6H_5 \quad \Delta H = 463.6 \text{ kJ/mol} \quad (1)$$
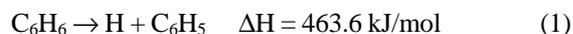
while the H_2 elimination and ring opening are the minor channels. Since the photon energy at 243.2 nm is 491.9 kJ/mol and the measured translational energy release in this experiment is 70.3 kJ/mol, the channel (1) cannot be opened by one photon absorption at 243.2 nm. Thus, it can be concluded that the H atom should be produced by the two photon process, which is also manifested by the linear slope of 4.2 from the power dependence in this experiment. Recently, the dissociation rate of benzene excited at 193 was measured to be $1 \times 10^5 \text{ s}^{-1}$.[10] The dissociation rates depend upon the internal energies after the internal conversion from the initially excited states to the ground state. The rate of dissociation at the energy of two photons at 243 nm was then calculated by the RRKM theory to be $0.2 \times 10^9 \text{ s}^{-1}$. The picosecond lifetime of the S_1 state and slow dissociation rate suggest the sequential two photon absorption process. The lifetime of benzene excited at 155 nm was also measured to be about 50 fs but in this case the decay is from the Rydberg states.[13] Thus, we conclude that the H atom is produced from the ground state after internal conversions from the initially excited Rydberg states by a nanosecond pulse of two photon absorption at 243.2 nm. The available energy that can be distributed among products is thus 519.6 kJ/mol, from which the fraction into product translation is 0.13. One peculiar observation to be noted is that the isotope effect in the dissociation of 1,3,5-benzene-d_3. The measured H/D ratio is 1.1, which should depend upon the rates of dissociation while the dissociation rate of H and D estimates the ratio of 1.4 because it depends upon the square root of the ratio of the reduced masses. One possible explanation is that the measured H/D ratio does not fully reveal the ratio of the rate constants because the measured H and D are generated in a rather short time interval. Since the dissociation rate depends upon the internal energy of the parent molecule and how this energy is distributed among the internal degrees of freedom, more refined calculations are required to explain the experimental results.

H from phenylacetylene: Photodissociation of phenylacetylene in UV has not been studied so far. The H and D atoms can be generated by the following primary processes.

$$C_6H_5C \equiv CD \rightarrow C_6H_4C \equiv CD + H \quad \Delta H = 468.6 \text{ kJ/mol} \quad (2)$$
$$\rightarrow C_6H_5C \equiv C + D \quad \Delta H = 566.1 \text{ kJ/mol} \quad (3)$$
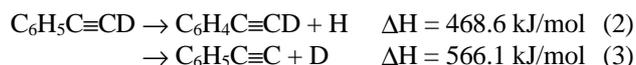
The photon energy at 243.2 nm is 491.9 kJ/mol, which can not open the channel (3) and the measured translational energy release in the channel (2) is 72.8 kJ/mol, which implies that both H and D atoms should be produced by the two photon process. Since the UV absorption in the acetylenic group to the π^* state starts from around 230 nm,[14] the initial one photon absorption can be assumed to the S_1 state

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of the phenyl group as in benzene followed by another photon absorption to the Rydberg states. Then, the fraction of the available energy into product translation in the case of H from phenyl group is 0.14 and D from acetylenic group is 0.17. The similar translational energy fractions for both channels and the measured H/D ratio of 5 imply a statistical dissociation assuming the isotope effect similar to the benzene dissociation case discussed above. Thus, as in benzene, it has been suggested that the H atoms are produced in the hot ground state *via* internal conversion from the initially excited state.

H from benzaldehyde: In the above discussion, it was suggested that the H atoms from benzene and phenylacetylene are produced in the ground state from the two photon absorption in the phenyl group followed by internal conversion. Thus, the H atoms from phenyl group may be generated by the same mechanism discussed above, which can also be manifested by the similar translational energy release to that of the benzene dissociation case. However, the D atom from the aldehyde group in benzaldehyde may come from different pathways. There are several possible primary processes in benzaldehyde upon two photon absorption in UV.

$$C_6H_5COD \rightarrow C_6H_4COD + H \quad \Delta H = 373.6 \text{ kJ/mol} \quad (4)$$
$$\rightarrow C_6H_5CO + D \quad \Delta H = 445.6 \text{ kJ/mol} \quad (5)$$
$$\rightarrow C_6H_5 + COD \quad \Delta H = 397.1 \text{ kJ/mol} \quad (6)$$

Upon UV absorption in carbonyl compounds such as acetone, the α-cleavage due to the $n \rightarrow \sigma^*$ transition has been reported for many years.[15,16] However, the translational energy release for the D atom production channel was measured to be 82.7 kJ/mol, which implies that the D atom cannot be produced from (5) by one photon absorption. The two photon absorption followed by internal conversion as in the benzene case would produce D. In addition, the statistical dissociation would produce the H/D ratio to be about 5 as in phenylacetylene-*d*. The measured H/D ratio of 1.5, however, would imply different dissociation pathways for the D atom production. One possible dissociation mechanism is that the two photon absorption leads the parent molecule to the Rydberg state and the D atom is generated from the repulsive triplet state after the curve crossing. In this case, as in the other carbonyl compounds, the dissociation lifetime would be on the order of femtoseconds,[17] from which the translational energy release would be much larger than the measured. Thus, the following dissociation mechanism for the D atom production is suggested. The two photon absorption in benzaldehyde primarily produces phenyl and COD radicals which have large amount of internal energies. Then, COD in turn is decomposed into CO and D. The dissociation energy of COH into CO and H is 52.1 kJ/mol with the barrier of 89.5 kJ/mol. The potential energies along the minimum energy path for the dissociation are obtained by *ab initio* calculations using the 6-31G** basis at the MP2 level (Figure 4). Then, although the internal energies in the phenyl and COD were not measured in this experiment, the measured translational energy release of 82.7 kJ/mol would
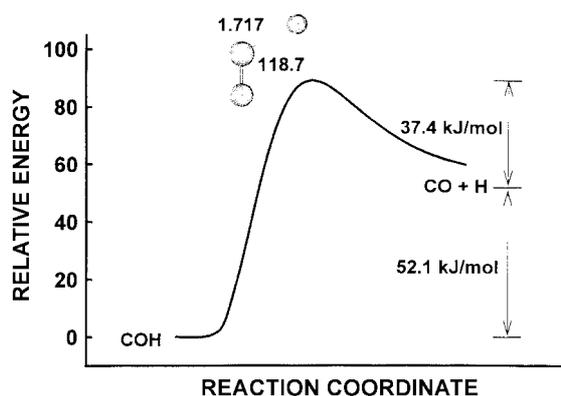

Figure 4. Potential energy curve along the minimum energy path obtained by *ab initio* calculations for the H atom elimination reaction from COH. The transition state geometry is depicted on top of the potential energy maximum.

be the 37.4 kJ/mol of energy of the reverse barrier which is transformed into product translation and the statistical partitioning of the remaining available energy.

Summary

The H atom channels from photodissociation of benzene, phenylacetylene, and benzaldehyde have been investigated. From the measured translational energy releases, it has been found that the H atoms are produced from two photon absorption at 243.2 nm. The H atoms from the phenyl group are produced in the ground electronic state after internal conversion while the H atom in the aldehyde group in benzaldehyde is produced from the secondary decomposition of COH, which is the primary product.

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